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VII.

AN INDIRECT DETERMINATION OF CHLORINE AND BROMINE BY ELECTROLYSIS.

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IN the indirect determination of chlorine and bromine the method most commonly employed is to precipitate both halogens with argentic nitrate, and then either to reduce the weighed argentic chloride and bromide to metallic silver by heating in an atmosphere of hydrogen, or to change the bromide into chloride by heating in a stream of chlorine gas.

The determination by either method is difficult, requires the closest attention, and is liable to give erroneous results; both on account of the slight loss that may occur in transferring the weighed chloride and bromide from the crucible to the glass tube, and also from slight volatilization during the heating. I have found that even in reducing the mixed haloids to metallic silver in a slow current of hydrogen, small particles of silver are almost always carried by the gas along the tube. Led by these facts, I attempted during the past winter to find a new method which would, if possible, from its accuracy and simplicity, tend to bring the indirect determination of chlorine and bromine when they occur in organic compounds more into vogue than is at present the case. In this attempt I believe I have been successful, and the method I have devised is based on the principle that melted argentic chloride and bromide are easily reduced to metallic silver by the galvanic current.

The details of the process are as follows:—

After the mixture of the two halogen compounds of silver has been heated in a porcelain crucible so that they just fuse together, the crucible is cooled and weighed, a piece of platinum foil connected with a platinum wire is placed in the crucible so that it rests on the melted silver salts, and dilute sulphuric acid (1 pt. conc. to 3 pts. water by

volume) is poured into the crucible until it is two-thirds full, a second piece of platinum foil united to a wire is then placed in the acid solution, care being taken that it does not touch the silver mixture. The zinc pole of a two-cell Bunsen battery is connected with the platinum foil that rests on the silver salts, and the carbon pole with the platinum foil just mentioned. The decomposition begins immediately, chlorine and bromine being given off from the positive electrode, the reduced silver remaining at the bottom of the crucible in the form of a porous mass. The reaction requires from twelve to eighteen hours; with a weight of less than one and a half grammes of the mixed haloids I have found twelve hours sufficient to produce complete reduction; with a weight exceeding that amount I prefer to allow eighteen. When the argentic chloride and bromide are completely reduced, the battery is disconnected, the electrodes taken out of the sulphuric acid solution and washed with distilled water. The sulphuric is then poured off from the silver, and the silver is washed by decantation with distilled water, the decanted liquid being poured through a small filter; this is afterwards burnt, added to the silver sponge which still remains in the crucible; the crucible is then heated over a low free flame to constant weight. The weight thus found, minus the weight of the crucible and filter ash, is of course the weight of silver contained in the argentic chloride and bromide.

The only point that requires any great degree of care in this process is the melting of the mixed haloids. The temperature at which the fusion takes place must be as low as possible, so as to avoid any volatilization, and the melted mass should be united as far as practicable in one piece.

In some of the following analyses I have used a platinum crucible. When this has been the case, one wire has been wound around the crucible, while the other, as before, has been merely allowed to dip into the acid solution; in this way the whole crucible serves as an electrode, and there is no need of bringing the melted chloride and bromide into one globule. With a platinum crucible, the washing of the reduced silver must be continued until a few drops of the filtrate gives no precipitate with baric chloride, and the drying should be done in an air bath at a temperature of about 150° C. After weighing, the silver, which always adheres to the crucible, can be dissolved out with dilute nitric acid.

The first series of analyses shows the accuracy of the process when either argentic chloride or bromide is taken alone, the second series when they occur together.

First series of analyses.

Wt. taken. Argentio chloride.	Wt. found. Silver.	Wt. calculated. Silver.
0.7206 grammes.	0.5419 grammes.	0.5425 grammes.
1.2984 "	0.9771 "	0.9777 "
1.8455 "	1.3892 "	1.3889 "
Wt. taken. Argentio bromide.	Wt. found. Silver.	Wt. calculated. Silver.
0.9313 grammes.	0.5352 grammes.	0.5350 grammes.
0.9421 "	0.5424 "	0.5424 "

In this connection I publish, by permission, three analyses, made according to this process, by Prof. J. P. Cooke, in determining the purity of a sample of argentic bromide.

Wt. of argentic bromide.	Wt. of silver.	Per cent of silver.
1. 4.1450 grammes.	2.3817 grammes.	57.444
2. 1.8172 "	1.0437 "	57.434
3. 4.9601 "	2.8497 "	57.449
Mean value . . .		57.442

Second series of analyses.

Wt. taken. Argentio bromide	Wt. taken. Argentio chloride.	Wt. found. Silver.	Wt. calculated. Silver.
0.9389 gr.	1.0498 gr.	1.3283 gr.	1.3293 gr.
1.0915 "	1.3042 "	1.6095 "	1.6086 "
1.1779 "	1.2551 "	1.6229 "	1.6217 "
1.2470 "	1.5420 "	1.8778 "	1.8770 "
1.6153 "	0.6661 "	0.8560 "	0.8550 "

The slight increase of variation between the found and calculated results in this second series of analyses I attribute to a slight volatilization of the argentic chloride before the chloride undergoes fusion.

With the argentic iodide I have only tried qualitative experiments, but I can see no reason why its determination when mixed with either argentic chloride or bromide cannot be accomplished according to this method.